

EFFECTS OF CATALYSTS AND CO₂ GASIFICATION ON THE ESR OF CARBON BLACK. II.

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INTRODUCTION

In a previous paper, we reported some preliminary results of an in situ esr study of a K₂CO₃-carbon black mixture as a function of temperature and steam gasification.^[1] We found that (1) heating the mixture in helium above 600 K produced irreversible broadening of the esr line, which did not occur for carbon black alone, (2) the broadened line had a shape broader than Lorentzian, and (3) under steam gasification conditions, the esr line width decreased in proportion to the steam concentration.

In the present paper, we report further results from in situ esr studies of (1) the thermal interaction between carbon black and various salts and (2) effect of CO₂ gasification conditions. Also, we used the esr technique^[2] to provide information on changes in the electrical conductivity of a sample that may relate to the mechanisms of the thermal and gasification reactions.

EXPERIMENTAL

The specifications of the carbon black (Spheron-6, Cabot Corporation) and the esr apparatus have been described.^[1] The samples consisted of a mixture of 3 wt% carbon black in a given salt that was mechanically ground with a mortar and pestle. The only diluent of the carbon black was a given salt. All the salts were of reagent quality. The amount of sample mixture examined by esr was adjusted so that a known mass of carbon black was present, between 3 and 6 mg.

Carbon dioxide gasification was performed by using premixed gases containing and 0, 4.1, 7.9, and 15.8 vol% CO₂ in helium. A switching valve was used to select the desired gas mixture to flow over the sample in the quartz reactor mounted in the high temperature esr sample heater.

The techniques for measuring changes in the relative electrical conductivity of a sample resulting from temperature changes or chemical changes have been described elsewhere.^[2] Briefly, a change in electrical conductivity of a sample is approximately proportional to two electrical conductivity parameters, ΔI_P^{-1} and ΔI_D , that can be measured during an esr measurement. I_P is the peak height of the resonance signal of a reference sample (0.1% pitch in KCl, Varian), which was situated in the auxiliary cavity of a dual rectangular cavity (TE₁₀₄); the sample was situated in the other cavity, which has the sample heater accessory. ΔI_P^{-1} calculated from the differences in the values of I_P^{-1} referring to two different conditions of the sample, e.g., temperature. I_D is the bias current of the crystal diode detector of the microwave bridge, and ΔI_D is the change in this current resulting from a change in the electrical conductivity of the sample. By connecting a recorder to the crystal diode current meter, it was possible to record ΔI_D as a function of time during gasification experiments. The parameter

ΔI_p^{-1} is suitable for measuring relatively large changes in electrical conductivity, such as those arising from heating a sample. The parameter ΔI_p is useful for following smaller changes in the electrical conductivity of a sample, e.g., arising from a chemical change associated with CO_2 gasification.

Free radical concentrations were measured by using a computer to store the esr data and to calculate the first moments of the first derivative curves. The results were normalized for cavity sensitivity using I_p , gain, rf modulation amplitude settings (typically 0.1 mT), and mass of carbon. Microwave power incident on the sample cavity was 1 mW.

RESULTS

For convenience, the results of the in situ esr measurements made on several salt-carbon black mixtures will be subdivided into two parts: thermal effects and CO_2 gasification effects.

Before each series of esr measurements with a given sample, oxygen was desorbed from the carbon by heating the sample in the esr reactor cell at about 500 K for 5 min while helium flowed through the cell. The value of the esr line width measured at room temperature was about 7.0 mT (70 gauss) before the desorption and about 0.15 mT after the desorption. The esr line was symmetric for all the salt-carbon black mixtures.

Various samples were tested for microwave power saturation, and none was detected for sample temperatures examined in the range from 290 to 800 K and for microwave power levels incident on the sample in the range of 0.1 to 40 MW; the upper value was limited by the electrical conductivity of the samples.

Thermal Effects

The thermal interaction between a salt and carbon black heated in helium were investigated by studying a series of potassium halide-carbon black mixtures. Alkali metal halides are less active catalysts than K_2CO_3 for gasification of carbonaceous materials.^[3,4] For comparison, a K_2CO_3 carbon black mixture was included. Also included was a mixture of carbon black with CaO which is expected to be a relatively poor gasification catalyst^[3,5] and has relatively low electrical conductivity at elevated temperatures. Hence, the CaO serves as a diluent to decrease microwave skin depth effects so that the esr properties of carbon black alone can be studied.

To determine the effects of heating the mixtures in helium we measured three esr parameters simultaneously: variations in the free radical concentration, line width, and ΔI_p . Measurements were made at successively higher temperatures (Figures 1a and 2a), but before progression to each next higher temperature, a measurement was made at 290 K (Figures 1b and 2b).

The free radical concentrations uncorrected for Curie's law were essentially independent of both the measurement temperature and the type of salt, within the accuracy of these measurements. The values of I_p , which were used to normalize the free radical concentrations for changes in cavity sensitivity, varied by a factor of about 10 over the temperature range studied, indicating the importance of such a correction.

The esr line width began to increase at temperatures above 850 K, and the magnitude of the increase was strongly dependent on the anion of the salt (Figure 1a). When the sample was cooled to room temperature the line width decreased. An irreversible effect is evident by the fact that a significant fraction of the line broadening produced at higher temperatures was retained upon cooling the samples (compare Figures 1a and 1b). In general, the effect on line width and the magnitude of the irreversible effects for the salts decreased in the following order: $\text{KBr} \approx \text{KCl} \approx \text{KI} > \text{K}_2\text{CO}_3 \approx \text{KF} > \text{CaO}$.

The electrical conductivity parameter, ΔI_p^{-1} , generally increased with heating temperature, and with few exceptions was almost independent of the type of salt mixed with carbon black (Figure 2a). The results of the measurements at 290 K, after cooling from a given higher temperature, also indicate that an irreversible increase in the electrical conductivity for some salts had been produced thermally (compare Figures 2a and 2b). Measurements on two salts, K_2CO_3 or KCl , in the absence of carbon black show that the ΔI_p^{-1} parameter has a very small temperature dependence, increasing less than 10% as the temperature was raised from 300 to 1200 K.

Comparison of Figures 1 and 2 suggests that there is a qualitative similarity in the way the heating temperature affects the two parameters, line width and ΔI_p^{-1} . A test of the relationship between line width and ΔI_p^{-1} is shown in Figure 3, which is a replot of the results in Figures 1a and 2a. The curves drawn in Figure 3 indicate that line width has a monotonic relationship to ΔI_p^{-1} , but that the functional dependence may be different for different salts.

CO_2 Gasification Effects

At elevated temperatures when He gas passing over a sample was switched to He containing CO_2 (15.8%), the line width decreased and the free radical concentration increased as shown in Figures 4 and 5, respectively. Before the CO_2 gasification measurements, the sample was thermally equilibrated at a given temperature for about 20 min. However, the line width and free radical concentration continued to change slowly, probably the result of slow irreversible changes caused by CO_2 as discussed above. Therefore, to separate the slow thermal changes from the rapid changes produced by CO_2 , we switched the gas flowing over the sample at a given temperature, 800 or 850 K, back and forth between He and He containing CO_2 . The sequence of the measurements is indicated by the numbers beside the data points in Figures 4 and 5. These results show that CO_2 had a greater effect at the higher temperature for both line width and free radical concentration. Also, at a given temperature the magnitude of the effect tended to become limited at concentrations of CO_2 greater than about 4%; e.g., see the line width dependence at 850 K in Figure 4. This behavior is probably due to a diffusion-limited process.

It was of interest to determine whether CO_2 gasification conditions altered the electrical conductivity of the sample, but the electrical conductivity parameter, ΔI_p^{-1} , exhibited a very small and almost imperceptible response. Therefore, the more sensitive electrical conductivity parameter, ΔI_D , was used. The recorded value of ΔI_D is shown in Figure 6, which shows the changes that occurred as the gas passing over the sample at 855 K was switched between He and 15.8 % CO_2 in He. Although the sample was initially in He the positive slope of ΔI_D indicates that the sample was not stable although it had been thermally equilibrated. However, it is clear from the recording that CO_2 caused the value of ΔI_D

to decrease (electrical conductivity decrease) and that subsequent exposure to He caused the value of ΔI_D to increase.

The observed values of the line width are marked in Figure 6 at three points in time. The results show that the line width changed reversibly when the sample was alternately exposed to He and CO_2 . Also, the decrease in line width correlates with the decrease in the electrical conductivity of the sample, as was the case in the study of thermal effects discussed earlier.

When carbon black alone and mixtures of carbon black with the potassium halides or with CaO were exposed to CO_2 gasification conditions at 850 K, very small or no changes were observed to occur in line width, free radical concentration, or in electrical conductivity (ΔI_D).

The correlation between an increase in the value of ΔI_D and an increase in electrical conductivity was established by noting that both ΔI_D and ΔI_P^{-1} changed in the same way for large enough changes in electrical conductivity, e.g., as produced by an increase of sample temperature.

DISCUSSION

In the previous paper^[1] some suggestions were made to account for those changes occurring in the esr spectra due to a thermal interaction between carbon black and K_2CO_3 and due to steam gasification. The additional experimental information obtained in the present esr study, pertaining to various other salts and a study of CO_2 gasification, provides a broader basis for interpreting the mechanisms of the thermal and gasification reactions.

Thermal Effects

Two mechanisms were suggested^[1] to account for the esr line broadening resulting from heating a mixture of salt and carbon black: (1) increased electrical conductivity and (2) unresolved hyperfine splitting (hfs) due to an interaction between the magnetic moment of the unpaired electron and that of the nucleus of the cation of the salt. The current results suggest that the increase in line width is related to the increase in the electrical conductivity because of the observed proportionality between the line width and the change in the electrical conductivity parameter for a series of salt-carbon black mixtures heated to various temperatures (Figure 3). In the following discussion, the relationship between these two parameters is examined in detail.

We postulate that some sort of complex is formed between certain salts and carbon black to account for the increase in the electrical conductivity and esr line width resulting from heating mixtures of salts and carbon black being significantly greater than the increase when the individual components are heated. Generally, an increase in electrical conductivity is due to an increase in the concentration or mobility of the charge carriers. Since the free radical concentration of the salt-carbon black mixtures was insensitive to temperature, it appears that charge carriers (conduction electrons or holes) are mainly responsible for the observed esr signal, whereas π -electrons would obey Curie's law. If the esr measurements detect all the charge carriers, then the observed increase of the electrical conductivity with increase in temperature is due mainly to an increase in charge carrier mobility.

We propose a series of reactions to account for the effect of the electronic properties of the solid. First, elemental metal atoms are produced by carbon reduction of the cation of the salt (e.g., K^+);^[6] Second, an extended aromatic structure develops by loss of hydrogen and polymerization of the carbonaceous material,^[7,8] and this polymerization could possibly be catalyzed by a salt or a metal atom. Third, a complex is formed between an aromatic structure and the ions or atoms of the salt. For example, such a complex could involve metal ions or atoms which (1) substitute for the hydrogens of CH or OH groups of the aromatic structure,^[9] (2) interact electrostatically with the π -orbitals of the extended aromatic structure,^[10] or (3) form a kind of intercalation compound with the available graphite-like structures, although such compounds are usually not expected to be stable at gasification temperatures.

For most salts studied, the changes in the esr parameters are largely irreversible, indicating that the salt-carbon black complex is stable. The greater effects produced by the alkali metal salts than by CaO or Al_2O_3 ^[1] are probably due to the greater ease with which carbon can reduce the alkali metal cations.

Based on the concepts suggested above, we propose that the observed line broadening results from relaxation effects that occur in the salt-carbon black complex when the unpaired electrons observed by esr experience the inhomogeneous fields developed near the sites at which a salt (e.g., the metal atom or cation and the anion) interacts with the aromatic carbon structure. Since these sites are nonuniformly distributed, the unpaired electrons in a conduction band or in π -orbitals experience different environments, resulting in inhomogeneous broadening of the esr line. The observed line shape, which is broader than Lorentzian, probably results from a superposition of two or more Lorentzian lines representing different environments.

Gasification Effects

Gasification by either steam^[1] or CO_2 of a salt-carbon black sample results in the same qualitative changes in the three esr parameters: a decrease in the line width, a decrease in the electrical conductivity, and an increase in the free radical concentration. Therefore, it appears that a single mechanism could account for the changes in the esr spectra that occur during gasification conditions.

We suggest that steam or CO_2 reacts with the salt-carbon complex and fragments carbon-carbon bonds of aromatic rings. As a result, the unpaired electrons will experience a decreased resonance path and less interaction with the atoms or ions of the salt that were associated with the aromatic ring before fragmentation. In other words, the unpaired electron will experience fewer regions with inhomogeneous fields, and therefore the esr line width should decrease.

Also as a result of the fragmentation of the aromatic rings the steady-state concentration of free radicals will be increased. Although these free radicals are probably unstable and will react with CO_2 or polymerize to produce a more stable structure, other radicals will be produced continuously by the gasification reaction.

The *in situ* esr results clearly indicate that for a salt to promote catalytic gasification, both the cation and anion of a salt must interact with the carbon structure. That is, switching to CO_2 gasification conditions caused changes in

the esr parameters only for salts with catalytic activity, e.g., salts with an alkali metal cation and a non-halide anion. Evidently, the character of the salt-carbon complex determines catalytic activity.

However, the changes in the esr parameters produced by thermal effects do not appear to correlate with the catalytic activity of the salts. For example, large increases in both line width and electrical conductivity occurred upon heating mixtures of carbon black with either of two salts, K_2CO_3 or KCl , which have widely different catalytic activities.

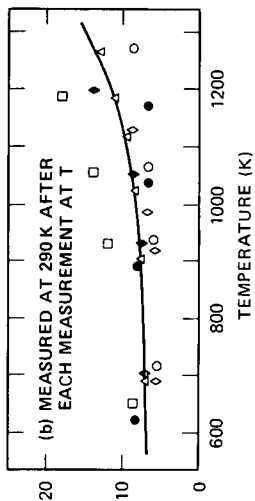
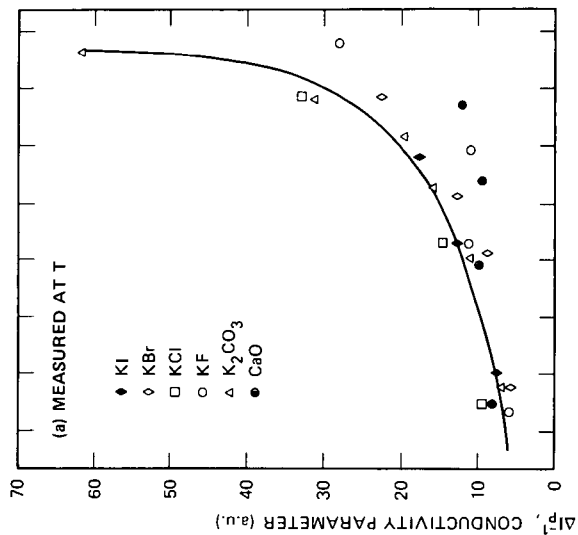
To elucidate the mechanism of catalytic gasification, we plan to consider the information developed by esr along with that obtained by other techniques being pursued in our laboratory.

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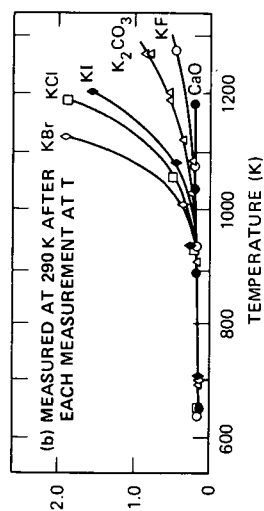
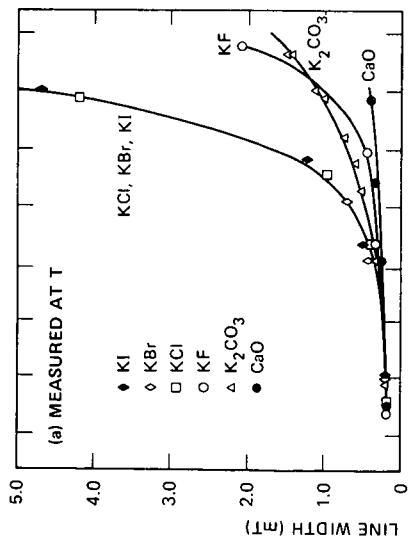
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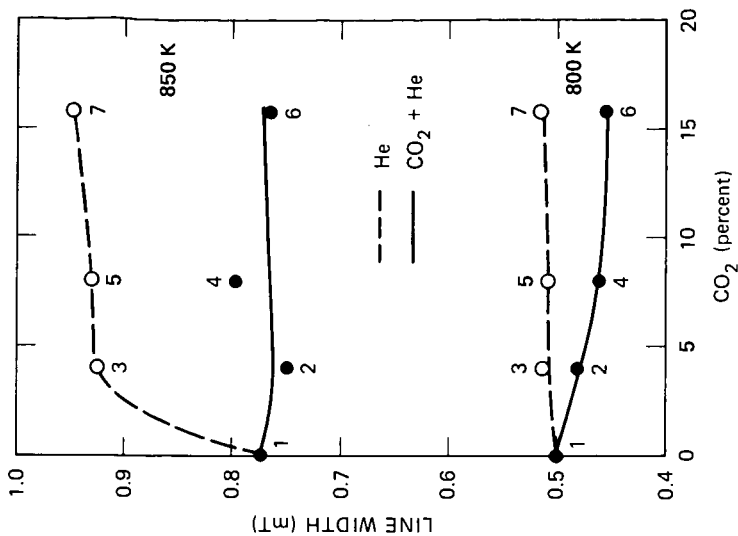
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FIGURE 2 EFFECT OF TEMPERATURE ON ESR ELECTRICAL CONDUCTIVITY PARAMETER OF SALT-CARBON BLACK MIXTURES
3 wt% carbon; heated in helium.



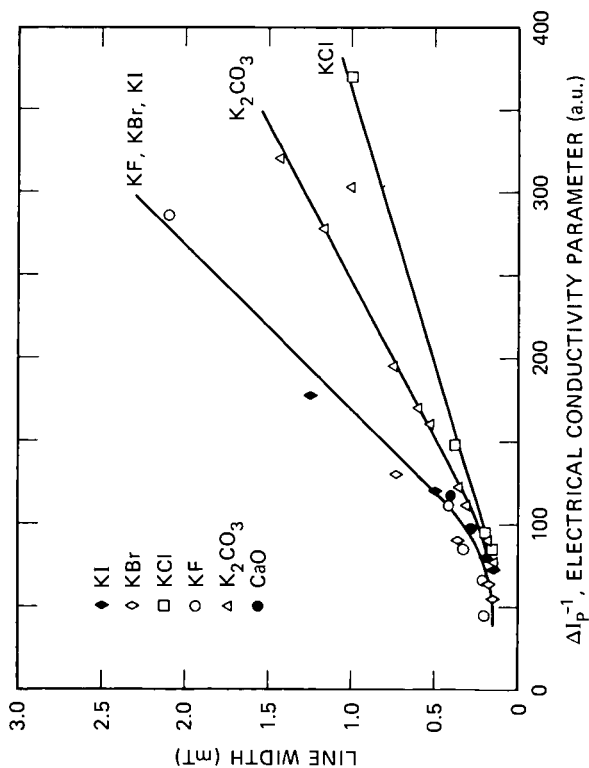
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FIGURE 1 EFFECT OF TEMPERATURE ON ESR LINE WIDTH OF SALT-CARBON BLACK MIXTURES
3 wt% carbon; heated in helium.



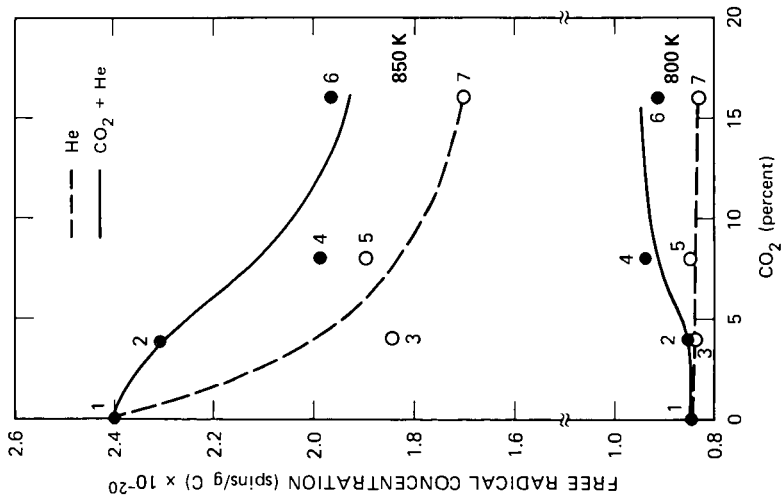
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FIGURE 4 EFFECT OF CO₂ ON ESR LINE WIDTH OF K₂CO₃-CARBON BLACK MIXTURE 3 wt% carbon; numbers identify sequence of measurements.



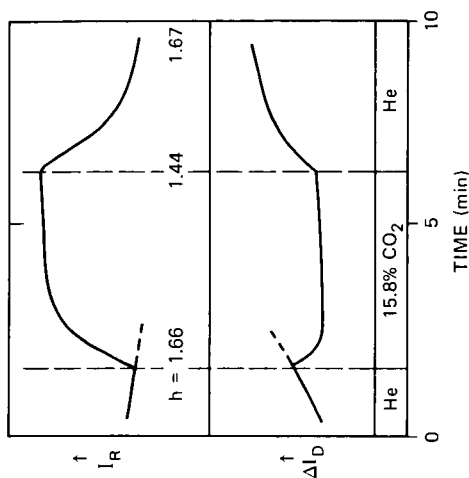
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FIGURE 3 RELATIONSHIP BETWEEN ESR LINE WIDTH AND ESR ELECTRICAL CONDUCTIVITY PARAMETER OF POTASSIUM SALT-CARBON BLACK MIXTURES 3 wt% carbon; heated in helium. Replot of Figures 2a and 3a.



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FIGURE 5 EFFECT OF CO₂ CONCENTRATION ON FREE RADICAL CONCENTRATION IN K₂CO₃-CARBON BLACK MIXTURE 3 wt% carbon; numbers identify sequence of measurements.



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FIGURE 6 EFFECT OF CO₂ GASIFICATION ON ESR PARAMETERS OF CARBON — K₂CO₃ (8 wt% K) MIXTURE AT 855 K
I_R — Peak intensity of radical signal
ΔI_D — Detector current
h — Line width (mT)